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• Graphical Abstract:

Meglumine catalyzed one-pot, three-component combinatorial synthesis of pyrazoles bearing a coumarin unit

Xiao-Tang Li, Yu-Heng Liu, Xin Liu, and Zhan-Hui Zhang*

Meglumine has been found to be an efficient catalyst for the synthesis of pyrazolylcoumarins by one-pot three-component reaction of salicylaldehyde, 4-hydroxy-6-methyl-2H-pyran-2-one, and hydrazine.
Meglumine catalyzed one-pot, three-component combinatorial synthesis of pyrazoles bearing a coumarin unit

Xiao-Tang Li\textsuperscript{a}, Yu-Heng Liu\textsuperscript{b}, Xin Liu\textsuperscript{a}, Zhan-Hui Zhang\textsuperscript{a,*}

A simple, efficient, and eco-friendly procedure for synthesis of a wide range of pyrazoles bearing a coumarin unit has been developed by one-pot three-component reaction of salicylaldehyde, 4-hydroxy-6-methyl-2\textit{H}-pyran-2-one, and hydrazine using meglumine as a catalyst in aqueous-ethanol media. This new protocol offers several advantages including the use of biodegradable and inexpensive catalyst, short reaction time, high yields, and simple work-up procedure.

Introduction

Currently, multicomponent reactions (MCRs) are becoming powerful and valuable synthetic strategy in modern organic and medicinal chemistry because they make multistep synthesis to be conducted in a single procedural step to provide novel and highly functionalized organic molecules and biologically active heterocyclic compounds from simple and readily accessible starting materials. These reactions hold the possibility for convenient, safe, atom-economic, high-yielding, and environmentally benign procedures and reduce generation of chemical waste.\textsuperscript{1-4} On the other hand, catalysts based on biodegradable materials such as chitosan,\textsuperscript{5} starch,\textsuperscript{6} cellulose,\textsuperscript{7} xanthan,\textsuperscript{8} polysaccharides,\textsuperscript{9} gluconic acid\textsuperscript{10} and eggshell\textsuperscript{11} have received much attention. Meglumine is an amino sugar derived from sorbitol and can be widely used in pharmaceuticals and medicine due to its peculiar physical and chemical properties such as low toxicity, bio-compatibility and bio-degradability, low cost and non-corrosion nature. It was early reported by Gu as a promoting medium with gluconic acid aqueous solution for hydroxymethylation of \(\beta\)-ketosulfones with formaldehyde.\textsuperscript{12} Meglumine contains amino group, primary and secondary hydroxyl groups. Therefore, it can activate the reaction components by not only base centers but also hydrogen bonding. Recently, it has been demonstrated that meglumine is a highly active catalyst for some organic transformations.\textsuperscript{13}\textsuperscript{13} Therefore, the combination of MCRs and meglumine will make the chemical reaction more economical and environmentally friendly.

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It is well known that pyrazole nucleus is an important core of various products and medicinal agents. They exhibit broad spectra of biological activities such as anticancer, antibacterial, antitubercular, antimicrobial, antioxidant, and kinase inhibitors. In addition, coumarins represent another important moiety occurring frequently in numerous natural products, pharmaceuticals, agrochemicals, dyes, and functional materials. Due to the importance of these two structural frameworks, the development of a simple procedure for the synthesis of aesthetically appealing molecular architecture containing both the pyrazole moiety and coumarin framework using biodegradable material as a catalyst and green solvent is still desirable and challenging task.

In view of the above points and as a continuation of our ongoing work on the development of multicomponent reactions and environmentally friendly methodologies, attempts were made to construct pyrazolylcoumarins via one-pot, three-component coupling (TCC) reaction of salicylaldehyde, 4-hydroxy-6-methyl-2H-pyran-2-one and hydrazine using meglumine as a biodegradable catalyst (Scheme 1).

![Scheme 1](image)

**Scheme 1** One-pot, three-component synthesis of pyrazolylcoumarins catalyzed by meglumine

**Results and discussion**

Initially, salicylaldehydes, 1,4-hydroxy-6-methyl-2H-pyran-2-one and phenylhydrazine served as model substrates for optimization of reaction conditions. Some of the key results are summarized in Table 1. In the control experiments, no anticipated product was observed in the absence any catalyst (Table 1, entries 1 and 2). Little product was obtained when the reaction was performed using Fe$_2$O$_3$ or L-proline as catalyst in a mixture of EtOH/H$_2$O. When CaCO$_3$, piperidine, 1,3-dimethylurea, chitosan, betaine HCl, mannitol, DMAP, Et$_3$N or DABCO was employed as the catalyst, the reaction took place, however, the yield of the target compound 4a was not satisfactory (entries 3-14). When the reaction was carried out in deep eutectic solvents (DES) such as choline chloride: urea or citric acid: DMU, no improvement was observed (entries 15 and 16). Further experiments found that meglumine was the best catalyst for this three-component reaction and afforded the desired product 4a in an isolated yield of 80% within 1.5 h (Table 1, entry 17).
Subsequently, the reaction media, amounts of catalyst and reaction times were also examined. The reaction did not proceed satisfactorily in water, possibly due to incomplete homogeneity of the reaction mixture. Further studies showed that aqueous-ethanol (1:1, v/v) was the best choice of solvent for this transformation. The reaction was also carried out using different amounts of the catalyst and the results showed that 20 mol% of catalyst was the best choice. Decreasing the amount of catalyst to 10 mol% relative to substrate, the yield of product decreased (entry 25). When the reaction was conducted with increasing amounts of meglumine or by prolonging the reaction times, the yield of $4a$ could not be further increased. From the above investigations, the optimized reaction conditions were established by employing salicylaldehyde, 4-hydroxy-6-methyl-2$H$-pyran-2-one (1 mmol), and phenylhydrazine (1 mmol) with meglumine (0.2 mmol) in aqueous-ethanol (1:1 v/v, 4 ml) under reflux for 1.5 h (Table 1, entry 17).

**Table 1** Optimization of the reaction conditions for the synthesis of $4a$.  

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Time (min)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>Ethanol</td>
<td>Reflux</td>
<td>720</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>None</td>
<td>Ethanol: H$_2$O (1:1)</td>
<td>Reflux</td>
<td>720</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Fe$_2$O$_3$</td>
<td>Ethanol: H$_2$O (1:1)</td>
<td>Reflux</td>
<td>720</td>
<td>Trace</td>
</tr>
<tr>
<td>4</td>
<td>L-Proline</td>
<td>Ethanol: H$_2$O (1:1)</td>
<td>Reflux</td>
<td>720</td>
<td>Trace</td>
</tr>
<tr>
<td>5</td>
<td>CaCO$_3$</td>
<td>Ethanol: H$_2$O (1:1)</td>
<td>Reflux</td>
<td>360</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>Piperidine</td>
<td>Ethanol: H$_2$O (1:1)</td>
<td>Reflux</td>
<td>360</td>
<td>40</td>
</tr>
<tr>
<td>7</td>
<td>1,3-Dimethylurea</td>
<td>Ethanol: H$_2$O (1:1)</td>
<td>Reflux</td>
<td>360</td>
<td>38</td>
</tr>
<tr>
<td>8</td>
<td>Chitosan</td>
<td>Ethanol: H$_2$O (1:1)</td>
<td>Reflux</td>
<td>360</td>
<td>35</td>
</tr>
<tr>
<td>9</td>
<td>Betaine HCl</td>
<td>Ethanol: H$_2$O (1:1)</td>
<td>Reflux</td>
<td>360</td>
<td>20</td>
</tr>
<tr>
<td>10</td>
<td>Mannitol</td>
<td>Ethanol: H$_2$O (1:1)</td>
<td>Reflux</td>
<td>360</td>
<td>30</td>
</tr>
<tr>
<td>11</td>
<td>DMAP</td>
<td>Ethanol: H$_2$O (1:1)</td>
<td>Reflux</td>
<td>360</td>
<td>42</td>
</tr>
<tr>
<td>12</td>
<td>DBU</td>
<td>Ethanol: H$_2$O (1:1)</td>
<td>Reflux</td>
<td>360</td>
<td>60</td>
</tr>
<tr>
<td>13</td>
<td>Et$_3$N</td>
<td>Ethanol: H$_2$O (1:1)</td>
<td>Reflux</td>
<td>360</td>
<td>56</td>
</tr>
<tr>
<td>14</td>
<td>DABCO</td>
<td>Ethanol: H$_2$O (1:1)</td>
<td>Reflux</td>
<td>360</td>
<td>68</td>
</tr>
<tr>
<td>15</td>
<td>Choline chloride: urea (1:2)</td>
<td></td>
<td>80</td>
<td>360</td>
<td>42</td>
</tr>
<tr>
<td>16</td>
<td>Citric acid: DMU (40:60)</td>
<td></td>
<td>80</td>
<td>360</td>
<td>30</td>
</tr>
<tr>
<td>17</td>
<td>Meclumine</td>
<td>Ethanol: H$_2$O (1:1)</td>
<td>Reflux</td>
<td>90</td>
<td>80</td>
</tr>
<tr>
<td>18</td>
<td>Meclumine</td>
<td>H$_2$O</td>
<td>Reflux</td>
<td>720</td>
<td>Trace</td>
</tr>
<tr>
<td>19</td>
<td>Meclumine</td>
<td>Glycerin</td>
<td>Reflux</td>
<td>720</td>
<td>40</td>
</tr>
<tr>
<td>20</td>
<td>Meclumine</td>
<td>Glycerin: ethanol (1:2)</td>
<td>Reflux</td>
<td>720</td>
<td>48</td>
</tr>
<tr>
<td>21</td>
<td>Meclumine</td>
<td>Glycerin: H$_2$O (1:3)</td>
<td>Reflux</td>
<td>360</td>
<td>56</td>
</tr>
</tbody>
</table>
Under the optimized reaction conditions, the scope of this three-component reaction was considerably expanded and the results are summarized in Figure 1. Various arylhydrazines bearing electron-donating group (EDG) and electron-withdrawing group (EWG) underwent the reaction with salicylaldehydes and 4-hydroxy-6-methyl-2H-pyran-2-one to afford the desired products in good to high yields. The influence of substituents on the benzene ring of phenylhydrazine was also examined. In general, substituents possessing an EDG tended to afford better yields than those bearing EWG. However, for phenylhydrazine with a strong EWG such as (4-nitrophenyl)hydrazine, no expected product was obtained. In addition to arylhydrazines, we found that hydrazine was compatible and furnished the desired product in good yield. The 2-hydrazinylpyridine worked well, providing high yield of expected. Fortunately, 2-hydrazinylbenzo[d]thiazole also proceeded efficiently, producing the corresponding product in 70% isolated yield.

Inspired by these encouraging results, we next explored the scope of this MCR process with respect to salicylaldehydes. As anticipated, salicylaldehydes bearing either electron-donating or electron-withdrawing groups such as hydroxyl, methoxy, NEt₂, chloro, bromo and nitro were all tolerated and afforded the respective products in good to high yields. Generally, the electron-withdrawing substituted salicylaldehydes showed better reactivity than the electron-donating substituted salicylaldehydes. Furthermore, 2-hydroxy-1-naphthaldehyde participated in the reaction smoothly and delivered the products 4ab-4ae in 70-86% yield, respectively.
A proposed mechanism for the synthesis of 3-(3-methyl-1-phenyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4a) from salicylaldehyde, 4-hydroxy-6-methyl-2H-pyran-2-one, and phenylhydrazine catalyzed by meglumine is shown in Scheme 2. We reasoned that in the presence of meglumine, Knoevenagel
condensation of salicyaldehyde and 4-hydroxy-6-methyl-2H-pyran-2-one would occur first to produce the intermediate I. The intermediate I could then undergo intramolecular cyclization by the nucleophilic addition of enolate oxygen to carbonyl group to afford the intermediate II. The intermediate II further reacted with phenylhydrazine to form the intermediate IV, which then tautomerized to intermediate IV. Finally, an intramolecular cyclization of intermediate IV promoted by meglumine would happen to give the target product 4a by eliminating one molecule of water.

![Diagram of plausible mechanism](image)

**Scheme 2.** Plausible mechanism for synthesis of product 4a.

**Conclusion**

In summary, a novel, highly efficient and green procedure has been successfully developed for the synthesis of a series of pyrazoles bearing a coumarin unit via one-pot three-component reaction of salicyaldehyde, 4-hydroxy-6-methyl-2H-pyran-2-one, and hydrazine by using meglumine as an inexpensive, biodegradable catalyst in aqueous-ethanol media. Environmental acceptability, economic viability, short reaction time, high yields, and cleaner reaction profiles are important features of this protocol. This strategy opens a new opportunity for the preparation of libraries of a wide variety of pyrazolylcoumarin derivatives for biological screening.

**Experimental section**

**General information**

All chemicals were purchased from commercial sources and used without further purification. Melting
points were determined using an X(4) apparatus and are uncorrected. IR spectra were taken as KBr discs with a Thermo Fisher Scientific Nicolet iS50 spectrometer. \(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker DRX-500 spectrometer at 500 MHz and 125 MHz in CDCl\(_3\), respectively. Elemental analyses were carried out on a Vario EL III CHNOS instrument. Mass spectra were recorded on a 3200 Qtrap instrument with an ESI source.

**General procedure for the synthesis of pyrazolesubstituted derivatives**

To a mixture of ethyl salicylaldehyde (1 mmol) and 4-hydroxy-6-methyl-2H-pyran-2-one (1 mmol) in ethanol-H\(_2\)O (1:1) (4 mL) was added hydrazine (1 mmol), and meglumine (0.2 mmol) at room temperature. The reaction mixture was stirred under reflux and monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature. The solid product was separated, washed with ether and purified by column chromatography on silica gel (eluent: EtOAc–hexane 1:9).

**Characterization data**

3-(3-Methyl-1-phenyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4a). White solid, 130-131 °C (Lit. 126-127 °C); IR (KBr): 3032, 1780, 1680, 1620, 1500, 1465, 1386, 1012 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) ppm: 7.55-7.52 (m, 1H), 7.46 (s, 1H), 7.42-7.40 (m, 3H), 7.38 (s, 1H), 7.34-7.31 (m, 3H), 7.24 (d, \(J = 7.5\) Hz, 1H), 6.61 (s, 1H), 2.40 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) ppm: 157.0, 155.1, 153.1, 143.1, 139.6, 129.6, 121.2, 118.8, 117.4, 116.6, 116.4, 114.7, 114.5, 112.7, 28.9; Anal. Calcd for C\(_{19}\)H\(_{14}\)N\(_2\)O\(_2\): C, 75.48; H, 4.67; N, 9.27. Found: C, 75.65; H, 4.50; N, 9.44; ESI-MS: \(m/z = 303 (M+1)^+\).

3-(1-(2-Methoxyphenyl)-3-methyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4b). White solid, 191-192 °C; IR (KBr): 3015, 1738, 1661, 1613, 1516, 1453, 1389, 1163, 756, 693 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) ppm: 8.50 (s, 1H), 7.51 (d, \(J = 7.5\) Hz, 2H), 7.48 (t, \(J = 5.5\) Hz, 2H), 7.39 (d, \(J = 7.5\) Hz, 2H), 7.35 (d, \(J = 8.0\) Hz, 1H), 6.91 (s, 1H), 6.83 (s, 1H), 3.83 (s, 3H), 2.18 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) ppm: 160.1, 154.7, 148.8, 142.2, 136.3, 133.6, 131.0, 130.5, 129.5, 128.3, 127.9, 127.6, 126.9, 126.4, 125.8, 120.7, 117.3, 112.3, 29.7, 14.1; Anal. Calcd for C\(_{20}\)H\(_{16}\)N\(_2\)O\(_3\): C, 72.28; H, 4.85; N, 8.43. Found: C, 72.45; H, 4.68; N, 8.60; ESI-MS: \(m/z = 333 (M+1)^+\).

3-(3-Methyl-1-(o-tolyl)-1H-pyrazol-5-yl)-2H-chromen-2-one (4c). White solid, 149-150 °C; IR (KBr): 3119, 1745, 1638, 1612, 1496, 1454, 1398, 1165, 750, 709 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) ppm: 8.50 (s, 1H), 7.52 (t, \(J = 7.0\) Hz, 2H), 7.41 (t, \(J = 7.0\) Hz, 1H), 7.38 (s, 1H), 7.37 (d, \(J = 5.0\) Hz, 1H), 7.34 (d, \(J = 7.5\) Hz, 1H), 7.31 (d, \(J = 7.5\) Hz, 1H), 7.28 (d, \(J = 7.5\) Hz, 1H), 7.10 (s, 1H), 2.17 (s, 3H), 2.13 (s, 3H); \(^{13}\)C
NMR (125 MHz, CDCl$_3$) δ ppm: 160.1, 153.4, 145.2, 140.9, 138.5, 137.3, 136.1, 131.1, 129.5, 128.9, 127.7, 126.7, 124.5, 120.7, 119.7, 116.4, 107.0, 17.3, 11.5; Anal. Calcd for C$_{20}$H$_{16}$N$_2$O$_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 76.10; H, 4.93; N, 9.03; ESI-MS: m/z = 317 (M+1)$^+$.  

3-(3-Methyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4d). White solid, 164 °C; IR (KBr): 3001, 1767, 1654, 1630, 1496, 1460, 1384, 1048 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) δ ppm: 8.51 (s, 1H), 7.55 (d, $J = 7.5$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.40 (7.35 (m, 2H), 7.34 (s, 1H), 7.28 (d, $J = 7.5$ Hz, 2H), 7.24 (d, $J = 7.5$ Hz, 1H), 7.06 (s, 1H), 2.44 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ ppm: 160.0, 153.4, 145.2, 140.1, 137.4, 131.2, 129.0, 128.9, 128.1, 125.9, 124.5, 122.1, 120.6, 119.6, 116.4, 108.3, 21.4, 12.5; Anal. Calcd for C$_{20}$H$_{16}$N$_2$O$_2$: C, 75.93; H, 5.10; N, 8.86; ESI-MS: m/z = 317 (M+1)$^+$.  

3-(1-(3,4-Difluorophenyl)-3-methyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4e). White solid, 209(210 °C; IR (KBr): 3032, 1750, 1668, 1600, 1502, 1543, 1381, 1050, 700 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) δ ppm: 8.47 (s, 1H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.51 (t, $J = 8.0$ Hz, 1H), 7.41 (t, $J = 8.0$ Hz, 1H), 7.35 (d, $J = 8.0$ Hz, 1H), 7.30 (7.27 (m, 2H), 7.07 (s, 1H), 6.99 (s, 1H), 2.38 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ ppm: 159.9, 153.5, 150.2 (dd, $J_{FC} = 249.5$, 13.6 Hz), 149.9 (dd, $J_{FC} = 248.9$, 12.5 Hz), 145.9, 140.1, 137.8, 136.0 (dd, $J_{FC} = 8.0$, 3.5 Hz), 131.4, 128.2, 124.6, 120.9 (dd, $J_{FC} = 6.4$, 3.7 Hz), 120.2, 119.5, 117.6 (d, $J_{FC} = 18.5$ Hz), 116.4, 114.7 (d, $J_{FC} = 19.6$ Hz), 109.0, 12.5; Anal. Calcd for C$_{19}$H$_{12}$F$_2$N$_2$O$_2$: C, 67.45; H, 3.58; N, 8.28; Found: C, 67.62; H, 3.41; N, 8.45; ESI-MS: m/z = 339 (M+1)$^+$.  

3-(1-(4-Bromophenyl)-3-methyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4f). White solid, 212(213 °C; IR (KBr): 3013, 1724, 1661, 1494, 1454, 1340, 1070, 753, 690 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) δ ppm: 8.51 (s, 1H), 7.66 (d, $J = 8.5$ Hz, 2H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.54 (t, $J = 8.0$ Hz, 1H), 7.43 (d, $J = 8.5$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 1H), 7.31 (t, $J = 8.0$ Hz, 1H), 7.11 (s, 1H), 2.41 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ ppm: 160.0, 153.5, 150.2 (dd, $J_{FC} = 249.5$, 13.6 Hz), 149.9 (dd, $J_{FC} = 248.9$, 12.5 Hz), 145.9, 140.1, 137.8, 136.0 (dd, $J_{FC} = 8.0$, 3.5 Hz), 131.4, 128.2, 124.6, 120.9 (dd, $J_{FC} = 6.4$, 3.7 Hz), 121.8, 120.4, 119.6, 116.4, 108.9, 12.5; Anal. Calcd for C$_{19}$H$_{13}$BrN$_2$O$_2$: C, 59.86; H, 3.44; N, 7.35; Found: C, 60.03; H, 3.27; N, 7.52; ESI-MS: m/z = 381 (M+1)$^+$.  

3-(3-Methyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4g). White solid, 180-181 °C (Lit. 182 °C$^{23}$; IR (KBr): 3432, 2954, 1728, 1713, 1610, 1554, 1459, 1394, 1032 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) δ ppm: 8.03 (d, $J = 7.5$ Hz, 1H), 7.53 (d, $J = 7.0$ Hz, 1H), 7.43 (s, 1H), 7.03 (t, $J = 8.5$ Hz, 1H), 6.98 (d, $J = 7.0$ Hz, 1H), 6.91 (s, 1H), 2.27 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ ppm: 159.8, 150.9, 146.0, 135.5, 131.1, 127.8, 125.2, 123.4, 117.8, 114.4, 32.0; Anal. Calcd for C$_{13}$H$_{16}$N$_2$O$_2$: C, 69.02; H, 4.46; N, 12.38; Found: C,
3-(3-Methyl-1-(pyridin-2-yl)-1H-pyrazol-5-yl)-2H-chromen-2-one (4h). White solid, 158-160 °C; IR (KBr): 3018, 1735, 1640, 1600, 1593, 1475, 1384, 1054 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ ppm: 8.18 (d, J = 4.5 Hz, 1H), 7.94 (s, 1H), 7.65 (t, J = 7.0 Hz, 1H), 7.55-7.51 (m, 1H), 7.37-7.33 (m, 1H), 7.19 (d, J = 7.5 Hz, 1H), 7.08 (s, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H), 6.84 (t, J = 6.0 Hz, 1H), 2.17 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ ppm: 157.2, 155.5, 147.8, 147.2, 142.9, 139.2, 138.6, 130.5, 129.8, 119.6, 118.2, 116.7, 116.4, 106.6, 30.9; Anal. Calcd for C₁₈H₁₃N₃O₂: C, 71.28; H, 4.32; N, 13.85. Found: C, 71.45; H, 4.15; N, 14.02; ESI-MS: m/z = 227 (M+1)⁺.

7-Methoxy-3-(3-methyl-1-phenyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4i). Yellow oil; IR (KBr): 3047, 1726, 1604, 1504, 1458, 1383, 1074, 1003, 776, 703 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ ppm: 8.48 (s, 1H), 7.75-7.73 (m, 1H), 7.56-7.54 (m, 1H), 7.54-7.53 (m, 3H), 7.48-7.44 (m, 2H), 7.06 (s, 1H), 6.89 (s, 1H), 3.91 (s, 3H), 2.40 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ ppm: 162.6, 155.3, 145.8, 140.0, 137.9, 132.3, 130.9, 129.2, 129.1, 128.8, 127.9, 125.1, 112.9, 108.2, 100.4, 65.6, 19.2; Anal. Calcd for C₂₀H₁₆N₂O₃: C, 72.28; H, 4.85; N, 8.43. Found: C, 72.45; H, 4.68; N, 8.60; ESI-MS: m/z = 304 (M+1)⁺.

6-Methoxy-3-(3-methyl-1-(o-tolyl)-1H-pyrazol-5-yl)-2H-chromen-2-one (4j). White solid, 148-150 °C; IR (KBr): 3003, 1742, 1663, 1609, 1514, 1454, 1333, 1088, 778, 700 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ ppm: 8.09 (s, 1H), 7.71 (d, J = 9.0 Hz, 2H), 7.53 (d, J = 8.5 Hz, 1H), 7.48 (d, J = 7.5 Hz, 1H), 7.44 (d, J = 7.5 Hz, 1H), 7.17 (t, J = 7.0 Hz, 2H), 7.09 (s, 1H), 3.85 (s, 3H), 2.40 (s, 3H), 2.31 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ ppm: 161.7, 153.2, 151.9, 150.5, 149.6, 145.7, 140.0, 138.1, 137.1, 132.3, 131.6, 130.9, 128.8, 127.2, 126.2, 122.4, 117.7, 113.3, 29.7, 19.2, 13.7; Anal. Calcd for C₂₁H₁₈N₂O₃: C, 72.82; H, 5.24; N, 8.09. Found: C, 72.99; H, 5.07; N, 8.26; ESI-MS: m/z = 347 (M+1)⁺.

7-Methoxy-3-(3-methyl-1-(m-tolyl)-1H-pyrazol-5-yl)-2H-chromen-2-one (4k). White solid, 163-165 °C; IR (KBr): 3007, 1735, 1700, 1631, 1507, 1465, 1384, 1049, 728, 695 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ ppm: 7.61 (s, 1H), 7.58 (d, J = 8.5 Hz, 1H), 7.53-7.51 (m, 3H), 7.48 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 8.5 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 6.65 (s, 1H), 3.81 (s, 3H), 2.43 (s, 3H), 2.29 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ ppm: 159.3, 151.8, 146.2, 139.1, 138.3, 130.8, 128.8, 126.7, 121.6, 117.9, 111.4, 111.0, 102.3, 29.7, 21.8, 12.8; Anal. Calcd for C₂₁H₁₈N₂O₃: C, 72.82; H, 5.24; N, 8.09. Found: C, 72.99; H, 5.07; N, 8.26; ESI-MS: m/z = 347 (M+1)⁺.

3-(1-(3,4-Difluorophenyl)-3-methyl-1H-pyrazol-5-yl)-7-methoxy-2H-chromen-2-one (4l). Yellow oil; IR (KBr): 3103, 1739, 1658, 1610, 1520, 1454, 1398, 1025, 777, 697 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ
ppm: 7.57 (s, 1H), 7.46-7.38 (m, 1H), 7.11 (d, J = 9.0 Hz, 2H), 7.11 (d, J = 5.5 Hz, 1H), 6.86 (d, J = 8.5 Hz, 1H), 6.82-6.81 (m, 1H), 6.46 (s, 1H), 3.88 (s, 3H), 2.36 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ ppm: 163.6, 159.2 (dd, $J_{FC}$ = 274.7, 13.2 Hz), 158.1 (dd, $J_{FC}$ = 252.9, 10.5 Hz), 155.8, 150.0, 142.9, 138.1, 137.2, 129.2 (dd, $J_{FC}$ = 10.4, 3.1 Hz), 120.2 (dd, $J_{FC}$ = 6.4, 3.7 Hz), 117.5 (d, $J_{FC}$ = 17.7 Hz), 115.0, 114.0 (d, $J_{FC}$ = 20.0 Hz), 113.3, 112.9, 112.1, 110.2, 108.7, 55.9, 13.5; Anal. Calcd for C$_{20}$H$_{14}$F$_{2}$N$_{2}$O$_{3}$: C, 65.22; H, 3.83; N, 7.61. Found: C, 65.39; H, 3.66; N, 7.78; ESI-MS: m/z = 369 (M+1)$^+$.  

**3-(1-[(4-Chloro-2-hydroxyphenyl)-3-methyl-1H-pyrazol-5-yl]-7-methoxy-2H-chromen-2-one (4m).** Yellow oil; IR (KBr): 3431, 2919, 1730, 1661, 1622, 1558, 1476, 1384, 1075, 715 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) δ ppm: 8.60 (s, 1H), 7.62 (m, 3H), 7.33 (m, 1H), 6.98 (s, 1H), 6.90 (d, $J = 7.5$ Hz, 1H), 6.83 (s, 1H), 3.91 (s, 3H), 2.71 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ ppm: 164.9, 158.4, 156.8, 146.0, 145.6, 142.2, 134.2, 131.8, 130.8, 129.1, 128.8, 118.3, 118.1, 116.9, 113.7, 112.4, 100.9, 100.2, 56.0, 27.2; Anal. Calcd for C$_{20}$H$_{15}$ClN$_{2}$O$_{4}$: C, 62.75; H, 3.95; N, 7.32. Found: C, 62.92; H, 3.78; N, 7.49; ESI-MS: m/z = 383 (M+1)$^+$.  

**3-(1-(Benzo[d]thiazol-2-yl)-3-methyl-1H-pyrazol-5-yl)-7-methoxy-2H-chromen-2-one (4n).** Yellow oil; IR (KBr): 3047, 1754, 1676, 1601, 1476, 1384, 1075, 715 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) δ ppm: 8.53 (s, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.11 (s, 1H), 6.90 (d, $J = 9.0$ Hz, 2H), 6.87 (s, 1H), 6.84-6.83 (m, 1H), 3.91 (s, 3H), 2.88 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ ppm: 159.5, 154.7, 151.9, 147.8, 145.8, 141.6, 140.4, 139.3, 133.9, 130.9, 128.5, 126.3, 124.1, 122.7, 119.0, 117.3, 106.1, 22.7, 14.1; Anal. Calcd for C$_{21}$H$_{15}$N$_{3}$O$_{3}$S: C, 64.77; H, 3.88; N, 10.79. Found: C, 64.94; H, 3.71; N, 10.96; ESI-MS: m/z = 390 (M+1)$^+$.  

**7-Hydroxy-3-(3-methyl-1-phenyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4o).** White solid, 150(151 °C; IR (KBr): 3489, 3125, 1722, 1646, 1601, 1496, 1449, 1384, 1075, 750, 687 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) δ ppm: 7.30 (m, 5H), 7.24 (m, 3H), 6.89 (s, 1H), 6.87 (s, 1H), 1.62 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ ppm: 156.0, 143.0, 139.2, 134.7, 147.1, 145.8, 142.6, 141.6, 140.4, 139.3, 133.9, 130.9, 128.5, 126.3, 124.1, 122.7, 119.0, 117.3, 106.1, 22.7, 14.1; Anal. Calcd for C$_{19}$H$_{14}$N$_{2}$O$_{3}$: C, 71.69; H, 4.43; N, 8.80. Found: C, 71.86; H, 4.26; N, 8.97; ESI-MS: m/z = 319 (M+1)$^+$.  

**3-(3-Methyl-1-phenyl-1H-pyrazol-5-yl)-6-nitro-2H-chromen-2-one (4p).** White solid, 168-170 °C; IR (KBr): 3489, 3125, 1722, 1646, 1601, 1496, 1449, 1384, 1075, 750, 687 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) δ ppm: 7.38 (s, 1H), 7.37 (s, 3H), 7.34-7.31 (m, 1H), 7.29 (t, $J = 4.5$ Hz, 1H), 7.25-7.24 (m, 1H), 7.23-7.21 (m, 1H), 7.00-6.97 (m, 1H), 6.62 (s, 1H), 2.38 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ ppm: 157.0, 155.1,
6-Chloro-3-(3-methyl-1-phenyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4q). White solid, 175-177 °C; IR (KBr): 3158, 1752, 1701, 1617, 1493, 1437, 1384, 1073, 713, 689 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ ppm: 7.94 (d, J = 8.0 Hz, 1H), 7.74 (m, 1H), 7.55 (m, 2H), 7.49 (s, 1H), 7.44 (t, J = 8.0 Hz, 2H), 7.37 (s, 1H), 7.09 (t, J = 8.5 Hz, 2H), 2.31 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ ppm: 156.9, 154.1, 149.6, 142.9, 140.9, 136.9, 134.7, 131.1, 127.8, 126.9, 122.6, 118.2, 117.6, 114.9, 112.1, 104.5, 21.0; Anal. Calcd for C₁₉H₁₃ClN₃O₄: C, 65.70; H, 3.77; N, 12.10. Found: C, 65.87; H, 3.60; N, 12.27; ESI-MS: m/z = 348 (M+1)⁺.

7-Chloro-3-(1-(2-methoxyphenyl)-3-methyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4r). White solid, 223(224 °C; IR (KBr): 3042, 1740, 1663, 1608, 1507, 1454, 1392, 1080, 778, 683 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ ppm: 8.41 (s, 1H), 7.47 (d, J = 7.5 Hz, 2H), 7.43 (d, J = 9.0 Hz, 1H), 7.38 (d, J = 7.5 Hz, 1H), 7.29 (d, J = 8.5 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.07-7.05 (m, 2H), 3.83 (s, 3H), 2.18 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ ppm: 154.6, 151.7, 145.0, 142.3, 135.8, 130.9, 130.7, 129.1, 127.1, 121.8 121.0, 120.8, 117.8, 112.1, 107.2, 29.7, 11.4; Anal. Calcd for C₂₀H₁₅ClN₂O₃: C, 65.49; H, 4.12; N, 7.64. Found: C, 65.66; H, 4.29; N, 7.81; ESI-MS: m/z = 367 (M+1)⁺.

6-Chloro-3-(3-methyl-1-((o)-tolyl)-1H-pyrazol-5-yl)-2H-chromen-2-one (4s). White solid, 150-151 °C; IR (KBr): 3095, 1740, 1661, 1602, 1502, 1454, 1380, 1083, 729, 690 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ ppm: 8.37 (s, 1H), 7.44 (s, 1H), 7.41 (t, J = 8.5 Hz, 2H), 7.38 (d, J = 9.0 Hz, 1H), 7.35 (d, J = 7.0 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 4.5 Hz, 1H), 7.06 (s, 1H), 2.14 (s, 3H), 2.08 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ ppm: 159.4, 151.7, 144.7, 141.0, 138.4, 136.0, 135.7, 131.2, 131.0, 129.7, 129.6, 127.7, 127.1, 126.8, 121.8, 120.7, 117.8, 107.2, 17.3, 11.5; Anal. Calcd for C₂₀H₁₅ClN₂O₂: C, 68.48; H, 4.12; N, 7.99. Found: C, 68.65; H, 4.14; N, 8.16; ESI-MS: m/z = 351 (M+1)⁺.

6-Chloro-3-(3-methyl-1-(m-tolyl)-1H-pyrazol-5-yl)-2H-chromen-2-one (4t). White solid, 167-169 °C; IR (KBr): 2923, 1731, 1608, 1592, 1495, 1479, 1370, 1032, 695, 649 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ ppm: 8.44 (s, 1H), 7.50-7.48 (m, 1H), 7.44 (d, J = 9.0 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.31 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 6.5 Hz, 1H), 7.24 (s, 1H), 7.06 (s, 1H), 2.44 (s, 3H), 2.37 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ ppm: 159.4, 157.8, 144.7, 140.5, 139.5, 136.3, 131.6, 129.8, 129.2, 129.0, 127.3, 126.0, 122.2, 121.4, 120.7, 117.8, 108.6, 21.4, 12.5; Anal. Calcd for C₂₀H₁₅ClN₂O₂: C, 68.48; H, 4.31; N, 7.99. Found: C, 68.65; H, 4.14; N, 8.16; ESI-MS: m/z = 351 (M+1)⁺.
6-Chloro-3-(1-(3,4-difluorophenyl)-3-methyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4u). White solid, 223-225 °C; IR (KBr): 3020, 1750, 1702, 1623, 1465, 1384, 1038, 717, 696 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ ppm: 8.40 (s, 1H), 7.53-7.52 (m, 1H), 7.46 (d, J = 8.5 Hz, 1H), 7.42-7.39 (m, 1H), 7.31 (d, J = 8.5 Hz, 2H), 7.23-7.17 (m, 1H), 7.08 (s, 1H), 2.39 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ ppm: 163.2 (dd, J_FC = 258.6, 11.1 Hz), 159.4 (dd, J_FC = 258.2, 14.5 Hz), 159.3, 151.8, 145.4, 140.3, 136.3, 131.3, 129.8, 127.3, 121.3, 121.0 (dd, J_FC = 6.4, 3.7 Hz), 120.6, 117.9 (dd, J_FC = 7.5, 3.1 Hz), 117.7 (d, J_FC = 18.5 Hz), 114.8 (d, J_FC = 19.6 Hz), 109.1, 12.5; Anal. Calcd for C₁₉H₁₁ClF₂N₂O₂: C, 61.22; H, 2.97; N, 7.52. Found: C, 61.39; H, 2.80; N, 7.69; ESI-MS: m/z = 373 (M+1)⁺.

3-(1-(4-Bromophenyl)-3-methyl-1H-pyrazol-5-yl)-6-chloro-2H-chromen-2-one (4v). White solid, 227 (229 °C; IR (KBr): 3030, 1745, 1666, 1600, 1505, 1454, 1403, 1363, 1313, 1298, 1273, 121.3, 121.0 (dd, J_FC = 6.4, 3.7 Hz), 120.6, 117.9 (dd, J_FC = 7.5, 3.1 Hz), 117.7 (d, J_FC = 18.5 Hz), 114.8 (d, J_FC = 19.6 Hz), 109.1, 12.5; Anal. Calcd for C₁₉H₁₂BrClN₂O₂: C, 54.90; H, 2.91; N, 6.74. Found: C, 55.07; H, 2.74; N, 6.91; ESI-MS: m/z = 415 (M+1)⁺.

6-Chloro-3-(3-methyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4w). White solid, 177-179 °C; IR (KBr): 3415, 3055, 1740, 1612, 1554, 1465, 1377, 1018, 731, 692 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ ppm: 8.55 (s, 1H), 7.62 (d, J = 2.0 Hz, 1H), 7.58-7.56 (m, 1H), 7.31 (d, J = 9.0 Hz, 1H), 7.00 (s, 1H), 2.27 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ ppm: 164.1, 157.4, 152.7, 144.0, 133.8, 130.3, 128.5, 127.2, 126.5, 121.9, 121.5, 120.6, 117.8, 109.1, 12.5; Anal. Calcd for C₁₃H₉ClN₂O₂: C, 59.90; H, 3.48; N, 10.75. Found: C, 60.07; H, 3.31; N, 10.92; ESI-MS: m/z = 261 (M+1)⁺.

6-Chloro-3-(3-methyl-1-(pyridin-2-yl)-1H-pyrazol-5-yl)-2H-chromen-2-one (4x). White solid, 168-169 °C; IR (KBr): 3415, 3055, 1740, 1612, 1554, 1465, 1377, 1018, 731, 692 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ ppm: 8.30 (d, J = 4.5 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.85 (t, J = 7.5 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.72-7.70 (m, 1H), 7.53-7.51 (m, 1H), 7.31 (s, 1H), 7.12-7.09 (m, 1H), 6.16 (s, 1H), 2.34 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ ppm: 156.9, 140.9, 138.0, 135.7, 131.1, 129.5, 129.2, 127.0 123.2, 121.7, 120.8, 119.9, 118.9, 116.4, 112.7, 101.4, 27.2; Anal. Calcd for C₁₈H₁₂ClN₃O₂: C, 64.01; H, 3.58; N, 12.44. Found: C, 64.18; H, 3.41; N, 12.61; ESI-MS: m/z = 338 (M+1)⁺.

7-Bromo-3-(3-methyl-1-phenyl-1H-pyrazol-5-yl)-2H-chromen-2-one (4y). White solid, 162-163 °C (Lit. 160-162 °C)³; IR (KBr): 3030, 1773, 1628, 1598, 1500, 1443, 1390, 1071, 748, 691 cm⁻¹; ¹H NMR
6-Bromo-3-(3-methyl-1H-pyrazol-5-yl)-2H-chroman-2-one (4z). White solid, 170-172 °C; IR (KBr): 3015, 1735, 1640, 1593, 1561, 1476, 1384, 1054, 780, 737, 700 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ ppm: 7.73 (s, 1H), 7.46 (s, 1H), 7.21 (d, J = 6.5 Hz, 1H), 7.16 (d, J = 5.5 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 2.06 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ ppm: 153.4, 152.5, 147.1, 142.2, 137.2, 136.3, 134.6, 134.3, 131.6, 131.2, 130.2, 129.1, 128.2, 126.4, 118.7, 118.5, 101.6, 15.3; Anal. Calcd for C₁₉H₁₀BrClN₂O₃: C, 52.87; H, 2.80; N, 6.49. Found: C, 53.04; H, 2.63; N, 6.66; ESI-MS: m/z = 413 (M⁺)⁺.

7-Bromo-3-(1-(4-chloro-2-hydroxyphenyl)-3-methyl-1H-pyrazol-5-yl)-2H-chroman-2-one (4aa). Yellow oil; IR (KBr): 3516, 2975, 1727, 1713, 1685, 1611, 1495, 1468, 1411, 1360, 1080, 770, 639 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ ppm: 8.41 (s, 1H), 7.93 (s, 1H), 7.74 (m, 1H), 7.71 (m, 1H), 7.47 (d, J = 5.0 Hz, 1H), 7.44 (s, 1H), 7.41 (s, 1H), 6.45 (d, J = 9.5 Hz, 1H), 2.71 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ ppm: 153.4, 152.5, 147.1, 142.2, 137.2, 136.3, 134.6, 134.3, 131.6, 131.2, 130.2, 129.1, 128.2, 126.4, 118.7, 118.5, 101.6, 15.3; Anal. Calcd for C₁₉H₁₂BrClN₂O₃: C, 52.87; H, 2.80; N, 6.49. Found: C, 53.04; H, 2.63; N, 6.66; ESI-MS: m/z = 413 (M⁺)⁺.

2-(3-Methyl-1-phenyl-1H-pyrazol-5-yl)-3H-benzo[f]chroman-3-one (4ab). White solid, 186-188 °C; IR (KBr): 3120, 1731, 1663, 1600, 1517, 1454, 1397, 1050, 740, 689 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ ppm: 8.77 (s, 1H), 8.37 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 9.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.49 (d, J = 9.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.39 (s, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.27 (s, 1H), 7.14 (s, 1H), 2.47 (s, 3H), 2.39 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ
ppm: 160.1, 153.0, 145.6, 140.1, 139.6, 139.4, 133.3, 132.5, 130.4, 129.3, 128.9, 128.8, 128.0, 126.0, 122.2, 119.6, 113.9, 108.4, 21.4, 12.5; Anal. Calcd for C_{24}H_{18}N_2O_2: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.84; H, 4.78; N, 7.82; ESI-MS: m/z = 367 (M+1)^+.

2-(3-Methyl-1-(2,4,6-trichlorophenyl)-1H-pyrazol-5-yl)-3H-benzo[f]chromen-3-one (4ad). White solid, 200-201 °C; IR (KBr): 3057, 1760, 1698, 1601, 1500, 1466, 1384, 1034, 778, 725 cm^{-1}; H NMR (CDCl_3, 500 MHz) δ ppm: 8.37 (d, J = 8.5 Hz, 1H), 8.07 (d, J = 9.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.46 (d, J = 9.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.31 (t, J = 8.0 Hz, 1H), 7.15 (s, 1H), 7.11 (s, 1H), 2.29 (s, 3H); 13C NMR (125 MHz, CDCl_3) δ ppm: 158.3, 141.1, 135.8, 129.8, 129.2, 129.1, 127.5, 126.6, 126.5, 126.3, 123.5, 121.8, 117.8, 116.5, 113.1, 109.5, 101.5, 27.4; Anal. Calcd for C_{24}H_{18}ClN_2O_2: C, 60.62; H, 2.88; N, 6.15. Found: C, 60.79; H, 2.71; N, 6.32; ESI-MS: m/z = 455 (M+1)^+.

2-(3-Methyl-1-(pyridin-2-yl)-1H-pyrazol-5-yl)-3H-benzo[f]chromen-3-one (4ae). White solid, 198-200 °C; IR (KBr): 3015, 1732, 1667, 1512, 1454, 1400, 1075 cm^{-1}; H NMR (CDCl_3, 500 MHz) δ ppm: 9.35 (s, 1H), 8.51 (t, J = 5.0 Hz, 1H), 8.46 (d, J = 8.5 Hz, 1H), 8.05 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.89 (t, J = 7.0 Hz, 1H), 7.71 (s, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.51 (d, J = 9.0 Hz, 1H), 7.48 (d, J = 9.0 Hz, 1H), 7.14 (s, 1H), 2.75 (s, 3H); 13C NMR (125 MHz, CDCl_3) δ ppm: 154.4, 147.8, 138.5, 138.4, 133.8, 131.0, 129.5, 129.0, 128.3, 127.9, 127.7, 126.3, 126.2, 125.8, 123.1, 121.7, 118.3, 116.7, 109.4, 14.1; Anal. Calcd for C_{22}H_{15}N_3O_2: C, 74.78; H, 4.28; N, 11.89. Found: C, 74.95; H, 4.11; N, 12.06; ESI-MS: m/z = 354 (M+1)^+.

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References


